Influence of the key parameters on the dynamic behavior of the hydrogen absorption by LaNi5

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Influence of the key parameters on the dynamic behavior of the hydrogen absorption by $LaNi_5$

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Abstract: *In this paper, a two-dimensional model of a closed metal–hydrogen reactor is presented. The temperature and the pressure temporal evolutions within the reactor as a function of time are reported. In order to determine the parameters to optimize a fast kinetic and optimal heat exchange, impact of the supply pressure, the porosity and the dynamic viscosity have been studied.*

1. Introduction

The metal hydrides provide a safe way of handling hydrogen. This is the most important point for hydrogen transportation and storage using metal hydrides. Therefore, an important number of studies has been carried out to develop this technology, and to improve the use of hydrogen in different applications such as fuel cell [1], heat pump [2], heat transformer [2], hydrogen compressor [2] and batteries [2]. This technology is great interest for transport application where the security, the weight and the volume are crucial factors when designing the vehicle. In order to describe the absorption and desorption process in porous media, various mathematical model have been reported on the heat and mass transfer [3-8]. A particular case, namely the hydride bed, have been studied in multiple investigations. Muthukumar P. et al [9] performed a parametric study of a hydrogen storage device in $MmNi_{4.6}Al_{0.4}$, they showed that the increase in the entire heat transfer coefficient is not of a positive impact. Most of presented models in the literature are based on symmetric axis tank 2D modeling, the first two-dimensional numerical studies of a hydrogen reactor was performed by A. Jemni et al [10]. Their results showed the importance of the geometry, the pressure at the inlet and the choice of the cooling temperature. Y.Kaplan et al [11] presented a mathematical model for the storage of hydrogen in solid form. As a conclusion of their work, they proved that rapid load requires efficient cooling which is directly related to the feed rate. In another study carried by K. B. Minko et al [3], the authors perform the analysis of a model of a cylindrical metal hydride tank. They conclude that the concentration gradient in the bed is the main driving force of the flow of hydrogen. Marty et al [12] have added an experimental validation of numerical simulations of hydrogen storage tank with metal hydrides, their goal was to obtain a better performance against the objectives set by a stationary cogeneration system. A numerical study of the heat and mass transfer in annular reservoir has been conducted in [13]. The results showed that the use of vanes improves the heat transfer and consequently an improvement of 40% of the time required for storage versus the case without fins. A computational fluid dynamics (CFD) model for the simulation of the storage of hydrogen in an activated carbon tank was described by R.

Shaheen et al. [14], this model showed that the amount of hydrogen adsorbed is greater than the one of the compressed hydrogen gas. A 3D modeling under Comsol & Multiphysics of a cylindrical tank was carried out in [15]. In order to determine the parameters of the hydride to optimize for optimal storage, their results showed that the most relevant parameters optimized are the load pressure, the permeability and thermal conductivity of the hydride. Brown et al. [16] developed a mathematical model describing the process of hydrogen storage in a commercial reservoir loaded with a metal hydride type AB2. The simulation has been carried out using Matlab. The obtained results allowed them to validate the experimental results and the simplifications made for reproducing the process of absorption and desorption of hydrogen by hydride.

The aim of this study is to determine the most parameters to optimize for a hydride tank. A simulation model was developed for analyzing the effect of certain parameters on the thermal behavior of the tank. To carry out the simulation, a mathematical model was done based on the Mass Conservation, momentum conservation and energy balance. The material used is $LaNi_5$. This paper will be organized as follows: First section presents the numerical model of the reactor, then, the governing equations of the model will be introduced. In section III, the simulation results of the heat and the mass transfer in the reactor are presented. The results obtained by changing some parameters are introduced in section IV. Finally, a conclusion of this work givens in section V.

2. Numerical model of the reactor

The physical model of the metal hydride reactor considered in this study is presented in figure 1. The reactor consists of a cylindrical container of radius R=10cm and height H=15cm. the considered geometry is axisymmetric half of the domain. It is surrounded by an aluminum frame in order to uniform the temperature. The cooling is performed by natural convection. The hydrogen is injected into the tank from the top at PH2inj pressure 8bar. The temperature is maintained constant at the inlet of the tank. The model is integrated and solved using Comsol Multiphysics 5.0

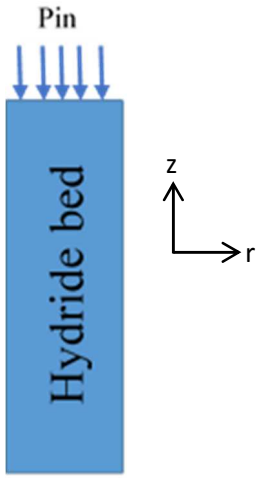


Figure.1. The geometry of the model

To simplify the model, the following assumptions are considered:

- The gas phase is ideal, from a thermodynamic point of view;
- The media are in local thermal equilibrium between gas and solid;
- The solid phase is isotropic and has a uniform and constant porosity;
- The radiative transfer in the porous medium are neglected;
- The reactor is considered in two dimensions;
- The flow is laminar (validity of Darcy's law);
- Hydrogen is supplied at the inlet to the bed at a known constant pressure P=8 bar.

The establishment of mathematical model describing the transfer of the heat and mass in porous media is directly inspired by methods that are traditionally used in mechanics of the continuous media. These methods consist of determining the local expression of conservation laws:

- Mass Conservation;
- Momentum Conservation;
- Energy conservation.

2.1. Energy equation

Add to the following assumption, the convective transfer can be neglected as well [19-21], also the temperature of the gaseous phase and the solid phase in the bed are similar (i.e local thermal equilibrium), the governing energy equation can be written as:

$$\left(\rho C_p\right)_{eff}\frac{\partial T}{\partial t}+\rho_g C_{pg} v_g \nabla T=\nabla\left(\lambda_{eff}\nabla T\right)+Sm \quad (1)$$

Where Sm is the source term given by

$$\mathrm{Sm}=(1-\varepsilon)|\Delta \mathrm{H}|\frac{\partial \rho_s}{\partial \mathrm{t}} \quad (2)$$

The effective heat capacity and effective$\left(\boldsymbol{\rho C_p}\right)_{\boldsymbol{eff}}$ thermal conductivity $\boldsymbol{\lambda_{eff}}$ of the hydride bed are expressed as:

$$\left(\rho C_p\right)_{eff}=\varepsilon\rho_g C_{pg}+(1-\varepsilon)\rho_s C_{ps} \quad (3)$$

$$\lambda_{\mathrm{eff}}=\varepsilon\lambda_{\mathrm{g}}+(1-\varepsilon)\lambda_{\mathrm{s}} \quad (4)$$

2.2. Masse balance

In order to model the hydrogen flow, the amount of hydrogen absorbed/ desorbed is determined using the mass conservation

For the gas, the mass conservation equation is:

$$\varepsilon\frac{\partial \rho_{\mathrm{g}}}{\partial \mathrm{t}}+\mathrm{div}\left(\rho_{\mathrm{g}}\vec{\mathrm{v}}_{\mathrm{g}}\right)=-\dot{\mathrm{m}} \quad (5)$$

For the solid, the mass conservation equation is:

$$(1-\varepsilon)\frac{\partial \rho_s}{\partial t}=\dot{m} \quad (6)$$

$$\rho_g=\frac{M_g P}{RT} \quad (7)$$

The gas velocity is given by Darcy's law:

$$\vec{v}_g=-\frac{K}{\mu}\overrightarrow{\nabla p} \quad (8)$$

Where:
K: the intrinsic permeability of the porous medium (m^2)
μ: dynamic viscosity of the fluid (Pa)

In order to validate Darcy law it is necessary to have a laminar flow, which is the case in porous media generally. The verification of this condition is done using the Reynolds number Re is defined as following:

$$R_e=\frac{QL}{v} \quad (9)$$

Where:
Q: flow rate [L / min]
L: the representative length of the flow [m]
v: Kinematic viscosity

The permeability K depends mainly on the solid while the viscosity μ depends on the nature of the fluid. It is given by the Kozeny-Carman equation. It describes the permeability as a function of grain size and porosity [17]:

$$K=\frac{d_p^2\varepsilon^2}{150(1-\varepsilon)^2} \quad (10)$$

Where
dp: diameters (m).
ε: Environmental porosity.

As for the dynamic viscosity, the majority of the works done in the literature do not take into account vis-à-vis changes in temperature. This dependence is expressed using the law of Sutherland:

$$\mu_{\mathrm{H2}}(\mathrm{T})=\mu_{\mathrm{H2}}(\mathrm{T_0})\left(\frac{\mathrm{T_0+C}}{\mathrm{T+C}}\right)\left(\frac{\mathrm{T}}{\mathrm{T_0}}\right)^{3/2} \quad (11)$$

With

$\mu_{H2}(T_0)$ is the dynamic viscosity at T_0

2.3. Kinetics reaction

The amount of the absorbed/desorbed hydrogen by the metal as a function of time is directly related to the rate reaction of the hydriding and dehydriding process. The absorption and desorption kinetics of a hydride indicate the speed with which the hydrogen is

absorbed by the intermetallic. They are strongly influenced by the thermodynamic conditions in the tank.

In absorption case:

$$\frac{\partial \rho_s}{\partial t} = C_a \exp\left(-\frac{E_a}{RT}\right) \ln\left(\frac{P}{P_{eq}}\right)(\rho_{ss} - \rho_s) \quad (12)$$

In desorption case:

$$\frac{\partial \rho_s}{\partial t} = C_d \exp\left(-\frac{E_d}{RT}\right) \frac{P - P_{eq}}{P_{eq}} \rho_s \quad (13)$$

Where Peq represents the equilibrium pressure that is given as a function of temperature. It is calculated using van't Hoff equation [14] for absorption case.

$$ln\left(\frac{P_{eq}}{P_0}\right) = A - \frac{B}{T} \quad (14)$$

Where A and B are Van't Hoff constants having values 12.919 and 3704.4 respectively [12].

The thermophysical proprieties of the $LaNi_5$ and hydrogen used to compute the model are listed in table 1:

Parameters	*Symbol*	*value*
Initial pressure	P0	1 [bar]
Activation energy	Ea	21170 [J/mol]
Universal gas constant	R	8.314 [J/mol/K]
Density of the solid at saturation state	ρ_ss	8520 [kg/m^3]
Density of the solid	ρ_0	8400 [kg/m^3]
Enthalpy of formation	ΔH	30 [KJ/mol]
Specific heat of the solid	Cps	419 [J/kg/K]
Specific heat of the H2	Cpg	14890 [J/kg/K]
Thermal conductivity of the solid	λs	2.4 [W/m/K]
Thermal conductivity of H2	λg	0.16 [W/m/K]
Dynamic viscosity of H2	µo	8.76 10-6 [Pa*s]
Reaction constant	Ca	59.9 [1/s]
Inlet temperature of hydrogen	T0	293[K]
Sutherland constant	c0	72
Porosity	ε	0.5
Inlet pressure of the hydrogen	Pin	8[bar]
Heat transfer coefficient	h	1650[W/m^2/K]

Table 1 : thermo physical properties of LaNi5, H2 and constant used in the analysis [14]

Initial and boundary conditions:

Initially at $t=t_0$, the temperature, the hydride density and the pressure in the reactor are assumed to be constant:

$$\text{So, for } t = t_0 \Rightarrow \begin{cases} T(t_0, r, z) = T_0 \\ \rho_s(t_0, r, z) = \rho_0 \\ P(t_0, r, z) = P_0 \end{cases}$$

The boundary conditions are expressed as

r=0 $\quad \frac{\partial P(0,z)}{\partial r} = 0;\ \frac{\partial \mathrm{T}(0,\mathrm{z})}{\partial \mathrm{r}} = 0$

z=0 $\quad \mathrm{T(r,0)=T0}$; $\mathrm{P(r,0)=P_{inj}}$

r=R $\quad \frac{\partial P(R,z)}{\partial z} = 0;\ \frac{\partial P(R,z)}{\partial z} = 0;$

$$\frac{\partial T(R,z)}{\partial r} = h(T - T_{ext})$$

z=H $\quad \frac{\partial P(r,H)}{\partial r} = 0;\ \frac{\partial \mathrm{T(r,H)}}{\partial \mathrm{r}} = 0$

3. Results

Figure 2 shows the average temperature as a function of time, which increases and reaches rapidly the maximum of the temperature. This increase of temperature is caused by the hydriding reaction of the intermetallic. After this rapid increase, the temperature decreases gradually up to reaching the cooling temperature to 293K. The system returns to its equilibrium state taking about one hour under the action of the convective exchange with the outside. The cooling time for the simulated reactor is quite high due to the low thermal conductivity of the hydride and the non-optimized thermal exchange.

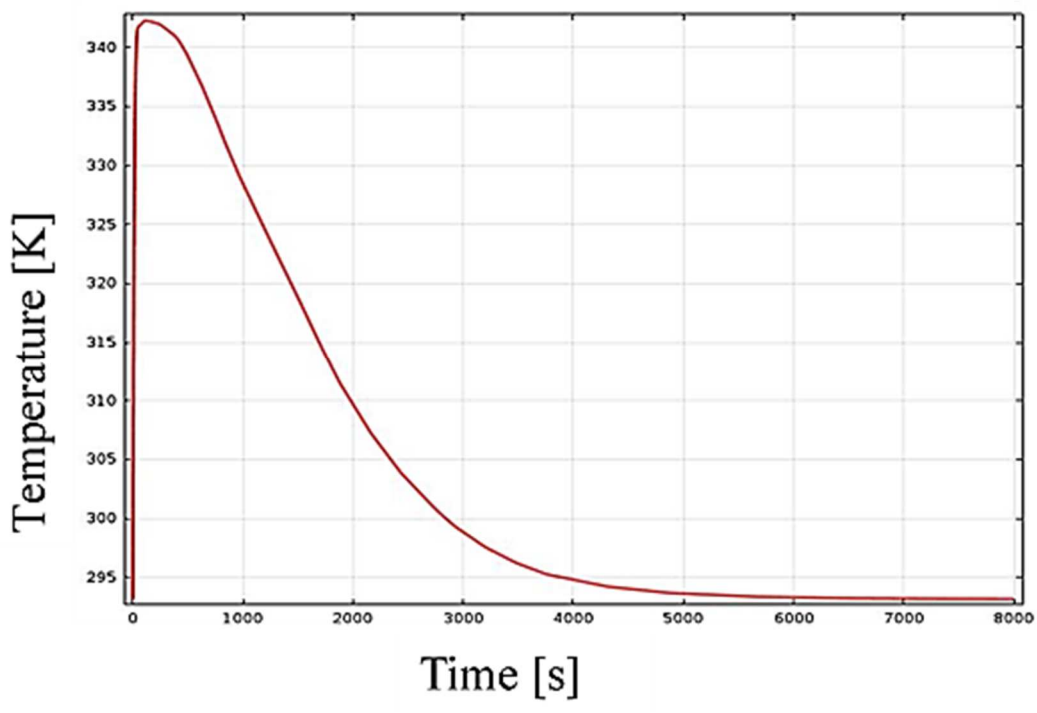


Fig.2. Bed temperature vs. time during absorption

In figure3, the evolution of the amount of hydrogen absorbed by the hydride versus time is represented. It is observed that the rate increase rapidly, due to a strong pressure gradient between equilibrium pressure and pressure applied, then the absorption rate stabilizes at a rate of 1.42% for the alloy concerned which is related to the pressure applied to its input.

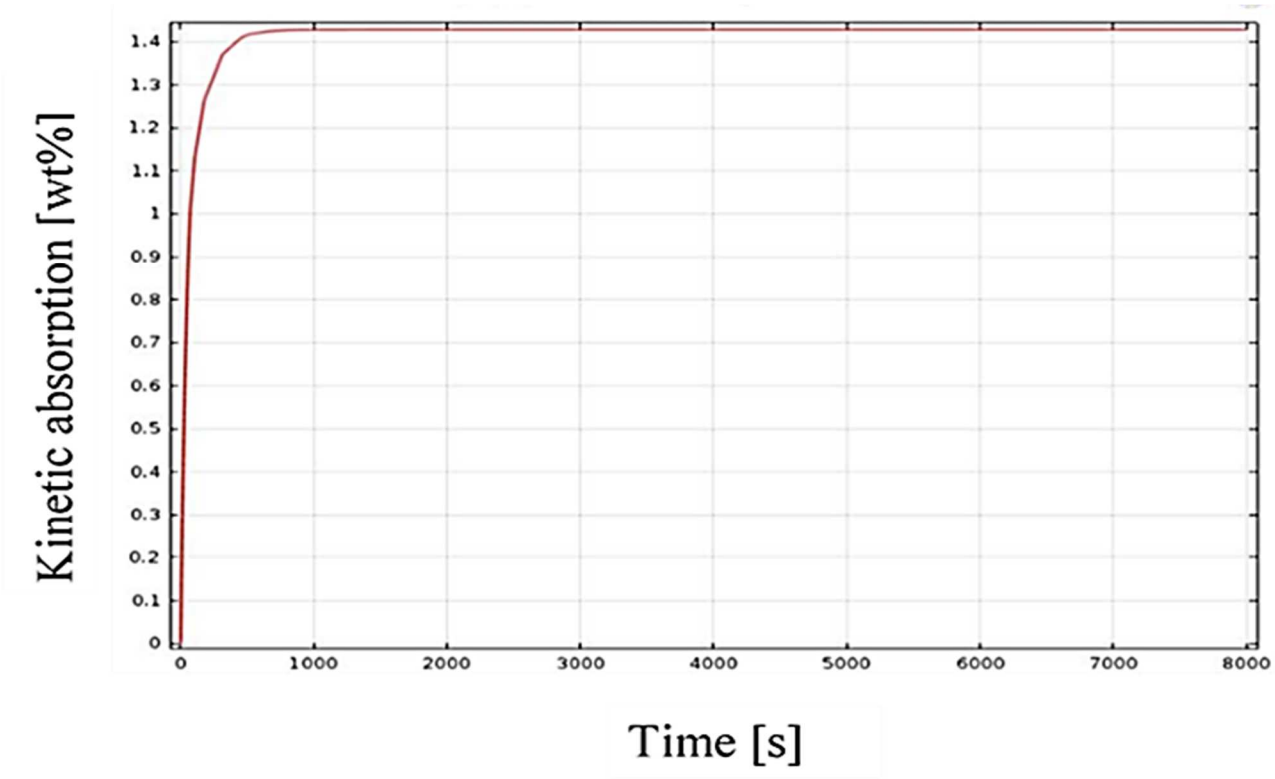


fig.3. concentration vs. time during hydrogen absorption

Figure 4 shows the variation in the bed temperature at various radial positions of the sensor in the tank. As it can be observed, the maximum temperature is reached rapidly in the majority of the bed, but, the time to return to thermal equilibrium is different according to the distance. This is due to the fact that, there is a high gradient of temperature and to the low thermal conductivity of the bed of hydride.

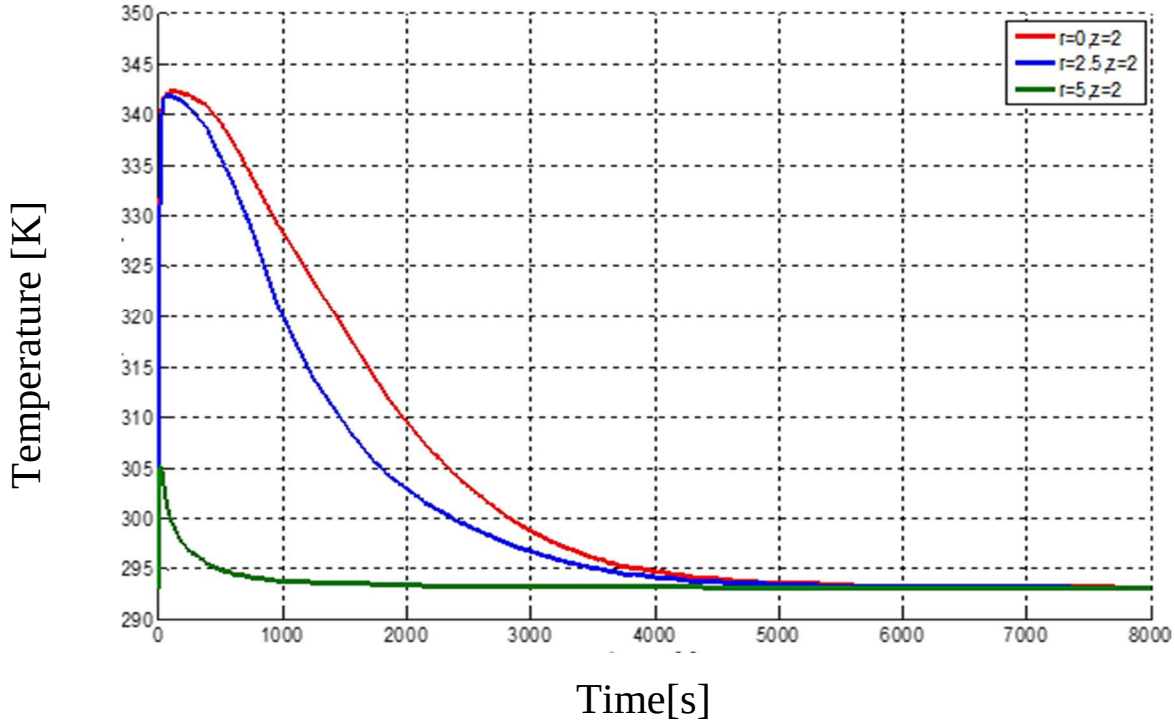


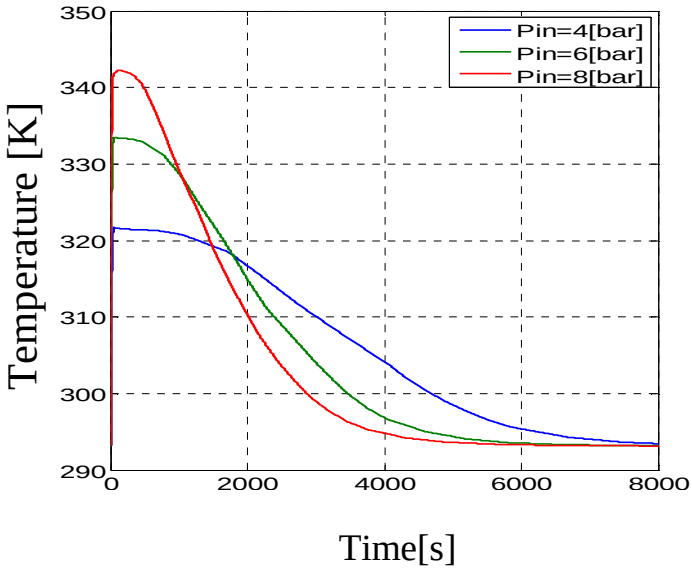
Fig.4. Bed temperature vs. time for various position in the reactor

4. Effect of certain parameters on the behavior of the tank.

4.1. Effect of the operating pressure

Figure 5 depicts the temporal evolution of the temperature and the atomic ratio within the reactor at different supply pressures, the temperature of the coolant is kept constant (20°C). As shown in figure 5a, the increase of the supply pressure makes the return of the system to the equilibrium state faster. It is also observed that, the rate of absorption reaches the maximum quickly for a high supply pressure Figure 5b.

(a)



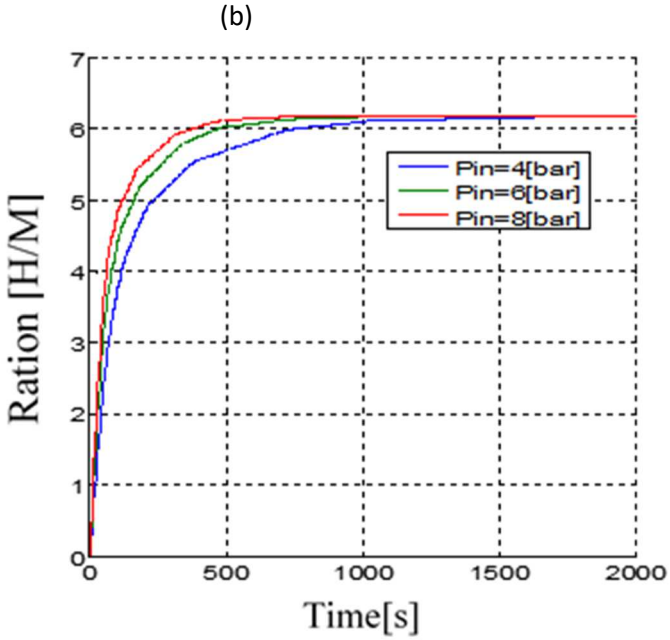


Fig.5. Effect of the supply pressure.

It can be noticed that the supply pressure has a direct impact on the kinetics but also on the heat exchange and the temperature gradient.

4.2. Effect of the grain size (Porosity).

Figure 6 shows the variation of the concentration with porosity. It is noticed that as the porosity increases the time to attain the equilibrium state is increased (absorption kinetics is nits). The main is that at low porosity, the effective conductivity is high hence the thermal gradient is lower and the thermal evacuated is faster.

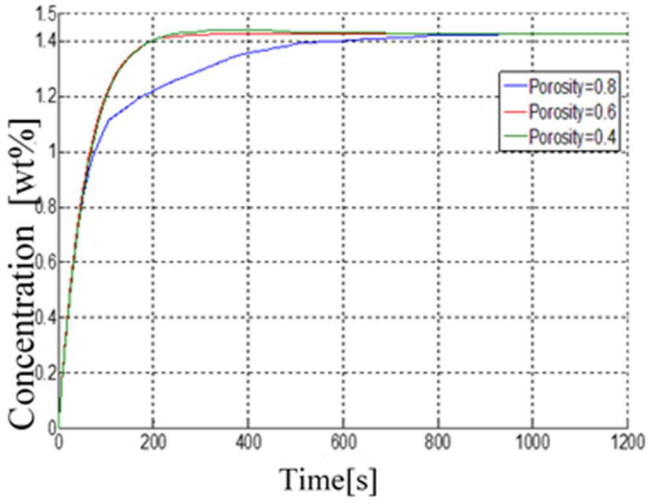


Fig.6. Effect of porosity

5. Conclusion

In this paper a numerical study is carried out for transient two-dimensional heat and mass transfer in cylindrical metal hydride bed. The numerical model developed takes into account the chemical aspects, thermodynamic, thermal fluids behavior of these reservoirs. The results showed a significant and rapid production of heat to the top of the absorption process of the hydrogen within the metal hydride. These temperature gradients between the center and the surface of the tank are axial and radial. The effect of different parameters such as supply pressure, porosity, temperature of the cooling fluid has been discussed and the results show that these parameters are crucial factors for an optimized tank design.

Furthermore, our results, although they are in accord with those available in the literature. This study should allow a design and manufacturing of optimal hydride tank for a better heat management between the metal-hydride tank and the fuel cell for drive-trains in automotive application.

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